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SYNTHESIS AND CHARACTERIZATION OF BINUCLEAR SCHIFF BASE 1/1  
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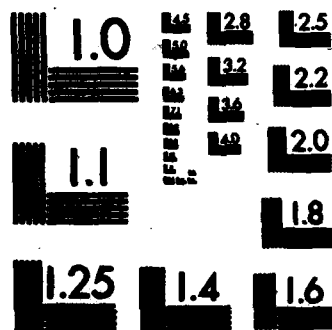


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Synthesis and Characterization of Binuclear  
Schiff Base Complexes of Nickel, Copper, and Manganese

by

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Synthesis and Characterization of Binuclear Schiff Base Complexes of Nickel,  
Copper and Manganese<sup>1</sup>

Bryan C. Whitmore and Richard Eisenberg<sup>2</sup>

Received

Binuclear complexes of Ni, Cu and Mn have been synthesized and characterized. The reaction of bis(salicylaldehyde) complexes of nickel(II) and copper(II) with *m*-xylylenbis-(2-(1,3-propanediamine)) (3) result in the formation of 1 and 2 respectively, while the reaction of manganese(II) acetate with salicylaldehyde and 3 results in the formation of 3a. The nickel complex, 1, undergoes a quasireversible two-electron transfer at -1.47 V vs SCE attributable to the nickel(II)-nickel(I) couple. The binuclear nickel(II) complex can be generated from 1 both electrochemically and chemically, and has been shown by infrared analysis to form adducts of CO and MeCN. Magnetic susceptibility measurements by the Faraday method show the manganese and copper complexes (3a and 2) have solid state room temperature moments of 5.47 and 1.92 B.M. per metal center, respectively, while the solution magnetic moment of the binuclear copper complex (2) is found by the Evans method to be 1.49 B.M. per copper center. This reduced magnetic moment relative to the moment for mononuclear Cu(salprn)(1.79 B.M.) suggests a weak magnetic interaction between the two copper centers in the binuclear copper complex 2. ←

Introduction

The synthesis of binuclear complexes in which a ligand structure maintains the metal centers in close proximity represents an important current objective in the study of transition metal systems. The interest in these complexes derives in part from their ability to serve as simple models for multi-metal-centered catalysts.<sup>2</sup> Many binuclear complexes of this type have been reported in recent years with the orientation of the metal centers, and hence, the nature of the metal-metal interactions, controlled via the selection of appropriate bridging ligands. Several series of complexes utilize ligands which hold the metals in close, fixed arrangements, as in the case of molecular A-frames,<sup>3</sup> cofacial diporphyrins,<sup>4</sup> side-by-side macrocycles<sup>5</sup> and macrocyclic inclusion complexes.<sup>6</sup> A different series of complexes employs more flexible ligands, which provide a less restricted environment for each metal relative to the second metal center. Examples of this series include so-called "wishbone complexes",<sup>7</sup> "ear-muff" complexes<sup>8</sup> and other similar complexes<sup>9</sup> which are based on ligands having bridging xylylene moieties. The binuclear complexes which we report in the present paper also belong to this last group of flexibly bridged binuclear metal systems.

By design, the metal centers in the binuclear complexes reported herein are separated by distances which vary from a minimum of 4 Å to a maximum of 12 Å. At the smallest of these values we expect no direct metal-metal bonding, although magnetic interactions between the metals in these complexes may be observable. More importantly, the complexes are constructed so that interactions between the two metal centers and a single substrate molecule, or between two metal-bound substrates are possible. These complexes, then, have the potential to serve as two-center, multielectron catalysts.

In the present paper we report the synthesis and characterization of

bimuclear nickel, manganese and copper complexes of the ligand *m*-xylidimbis-(2-(1,3-propanediol)ethylidene). Drawings of the bimuclear complexes, along with the nomenclature used throughout this paper are presented in Figure 1.

#### Experimental Section

Manipulations involving air sensitive materials were performed under nitrogen using modified Schlenk techniques. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

Physical Measurements. Melting points were determined using a Mel-temp apparatus and are uncorrected. <sup>1</sup>H NMR were recorded on a JEOL-CD M100 100 MHz instrument, a Varian EM-390 90 MHz instrument or a Bruker WM400 400 MHz instrument with chemical shifts reported in ppm relative to TMS as an internal standard. Deuterated solvents were purchased from Aldrich. Infrared spectra were recorded on a Perkin-Elmer model 467 grating spectrophotometer. Samples were either nujol mulls on NaCl plates or KBr pellets. Electronic spectra were recorded on a Perkin-Elmer model 330 spectrophotometer or a Cary model 118 spectrophotometer using 1 cm quartz cells. Extinction coefficients are given in l m<sup>-1</sup> cm<sup>-1</sup>. Solid state magnetic moments were determined by the Faraday method using a Cahn electrobalance and HgCo(NCS)<sub>4</sub> as a calibrant. Diamagnetic corrections were made using Pascals constants.<sup>10</sup> Solution magnetic moments were determined using the Evans NMR method<sup>11</sup> in DMSO-*d*<sub>6</sub>. Electrochemical measurements were made at room temperature using a PAR 173 potentiostat, PAR 175 universal programmer, and a PAR 179 Digital coulometer. The three electrode cell utilized a saturated calomel reference electrode with a .1 M KClaq salt bridge, and a platinum auxiliary electrode. For cyclic voltammetry the working electrode was either glassy carbon, platinum or a hanging mercury drop. Controlled potential coulometry required either a mercury pool or a platinum basked working electrode.

Reagents. Isophthalaldehyde was purchased from Tiedem Fluka. Malononitrile

was purchased from Aldrich and was distilled from  $P_2O_5$  at reduced pressure prior to use.  $BH_3$ -THF complex (1 M solution in THF) and salicylaldehyde were purchased from Aldrich. Benzylmalonitrile,<sup>13</sup> Hissalprn,<sup>14</sup> Hissalprn,<sup>15</sup> and  $\alpha$ -Cupalprn<sup>16</sup> were all prepared by the literature methods and gave satisfactory elemental analyses. Triethylamine/formic acid azeotrope (TEAF)<sup>17</sup> was prepared by the literature method. All solvents used were analytical reagent grade except where otherwise noted. THF was distilled from sodium-lead alloy and benzophenone under nitrogen.

m-Xylylbis(malonitrile) (1). Malonitrile (2.64 g, 0.04 m) dissolved in ethanol (10 ml) is added to a solution of isophthalaldehyde (2.76 g, 0.02 m) in hot ethanol (35 ml). The solution is heated 10 minutes, cooled to room temperature and filtered yielding **1** as a white crystalline solid (4.3 g, 93%). mp 177-179°C. Anal. Calcd for  $C_{14}H_{10}N_4$ : C, 73.03; H, 2.63; N, 24.34. Found: C, 72.96; H, 2.80; N, 24.36.  $^1H$  NMR ( $CD_3CO_2$ ): 8.2-8.5 (m, 5H, vinyl, 4,5,6-aromatics), 7.7-8.0 (m, 1H, 2-aromatic). IR (KBr):  $\nu_{CN}$ , 2225  $cm^{-1}$ . Mass spectrum  $m/e$  230 ( $M^+$ ).

m-Xylylbis(malonitrile) (2). A DMF solution (40 ml) of **1** (2.3 g, 0.01 m) and TEAF (5.2 g) is stirred at 35°C for two hours, added to ice water (40 ml) and extracted with benzene (3x100 ml). The benzene extracts are washed with water (200 ml), dried over  $MgSO_4$  and reduced in volume to 10 ml. The resulting precipitate is then recrystallized from hot ethanol (50 ml) giving **2** as a white crystalline solid (1.9 g, 81%). mp 120.5-122°C. Anal. Calcd for  $C_{14}H_{10}N_4$ : C, 71.77; H, 4.31; N, 23.92. Found: C, 71.64; H, 4.56; N, 23.87.  $^1H$  NMR ( $CD_3CO_2$ ): 7.4 (s, 4H, aromatic), 4.6 (t (J = 7 Hz), 2H,  $CH(CH_2)_2$ ), 3.4 (d (J = 7 Hz), 4H, benzylic). IR:  $\nu_{CN}$  2255  $cm^{-1}$ . Mass spectrum  $m/e$  234

( $M^+$ ).

p-Xylylbis(2-(1,3-propanediylamino)) (3).  $BH_3$ /THF (135 ml, 0.135 m) is added to a refluxing solution of **2** (6.38 g, 0.027 m) in THF (100 ml) under a nitrogen atmosphere over a period of 90 minutes. The solution is refluxed nine more hours and then cooled to room temperature. Concentrated HCl (12 ml) is cautiously added to the reaction solution and the solvent is removed in vacuo. To the solid residue, 16 M aqueous NaOH (45 ml) is slowly added. The solution is placed on a hot water bath 45 minutes, followed by cooling and filtration. Upon standing, the filtrate forms two layers. The top layer is removed, dissolved in methanol (150 ml) and filtered. Removal of solvent then yields crude **3** (5.8 g) Bulb-to-bulb distillation at 0.001 mm and 150°C yields **3** as a colorless oil (0.68 g, 10 %).  $^1H$  NMR ( $CD_3CO_2$ ): 7.04 (m, 4H, aromatic), 2.6 (m, 12H, all methylenes), 1.6 (m, 2H, methine). IR:  $\nu_{NH}$  3260, 3350  $cm^{-1}$ .

2-Benzyl-1,3-diaminopropane (4).  $BH_3$ /THF (82 ml, 0.082 m) is added over a ten minute period to a refluxing solution of benzylmalonitrile (5.3 g, 0.034 m) in THF (20 ml) under a nitrogen atmosphere. The reaction solution is refluxed four hours. Reaction workup is similar to the workup of **2**, using HCl (4.1 ml) and 16 M NaOH (20 ml). After basic hydrolysis and filtration, the aqueous phase is extracted with ether (3x30 ml) and the organic phase dried over magnesium sulfate and removed in vacuo. The remaining oil is vacuum distilled yielding **4** as a colorless oil. (0.9 g, 16%). bp 130-135°C (4 mm Hg).  $^1H$  NMR ( $CDCl_3$ ): 7.1 (s, 5H, aromatic), 2.4-2.7 (overlapping doublets, 6H, methylene, benzylic), 1.5-1.8 (m, 1H, methine), 1.1 (s, 4H,  $NH_2$ ). IR:  $\nu_{NH}$  3265, 3345  $cm^{-1}$ .

m-Xylylenebis(Nisalprn) (**5**). A suspension of bis(salicylaldehyde)nickel(II) dihydrate (0.95 g, 2.87 mm) and **3** (0.35 g, 1.4 mm) in 95% ethanol (100 ml) is refluxed 24 hours. The solvent is removed and the resulting olive green solid is dissolved in  $\text{CHCl}_3$  and filtered to remove unreacted  $\text{Ni(sal)}_2$ . Removal of  $\text{CHCl}_3$  yields **5** as a brown solid (0.91 g, 83%). Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{NiO}_4$ : C, 61.79; H, 5.20; Ni, 6.87; Ni, 14.38. Found: C, 61.27; H, 5.15; Ni, 6.52; Ni, 14.16. IR(KBr):  $\nu_{\text{C-N}}$  1610  $\text{cm}^{-1}$ ;  $\nu_{\text{aromatic}}$  1535  $\text{cm}^{-1}$ . UV/VIS(THF):  $\lambda_{\text{max}}$  600 nm (shoulder) ( $\epsilon$  136), 416 nm ( $\epsilon$  8000), 360 nm ( $\epsilon$  9000), 320 nm ( $\epsilon$  9000).  $\mu_{\text{eff}}$  0.31 B.M. (Faraday) (uncorrected).  $^1\text{H NMR}$  ( $\text{CDCl}_2$ ): 6.4-7.5 (m, 2H, aromatic, imine CH), 3.3-3.9 (m, 8H,  $\text{CH}_2\text{-N}$ ), 2.6-2.8 (m, 4H, benzylic), 2.3-2.6 (m, 2H, methine). ( $J_{\text{CH-N}}$  6.6 Hz,  $J_{\text{CH-C}}$  5.6 Hz,  $J_{\text{CH-N}}$  7.1 Hz,  $J_{\text{CH-C}}$  7.6 Hz,  $J_{\text{H-H}}$  6.2, 6.4 Hz,  $J_{\text{H-H}}$  7.6 Hz). See Figure 2 and Results Section for more detailed assignments.

m-Xylylenebis(Nisalprn) (**5a**). An aqueous solution (10 ml) of **3** (0.53 g, 2.12 mm) is added dropwise to a stirred solution of manganese(II) acetate dihydrate (1.04 g, 4.24 mm) and salicylaldehyde (1.03 g, 8.48 mm) in methanol (30 ml) under a nitrogen atmosphere. The resulting yellow precipitate is filtered under nitrogen and dried in vacuo yielding **5a** as a yellow solid (1.0 g, 60%). Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{MnO}_4$ : C, 61.01; H, 5.38; Mn, 6.78; Mn, 13.19. Found: C, 60.70; H, 5.33; Mn, 6.25; Mn, 12.68. IR(KBr):  $\nu_{\text{C-N}}$  1615,  $\nu_{\text{aromatic}}$  1535  $\text{cm}^{-1}$ .  $\mu_{\text{eff}}$  5.47 B.M./metal center (Faraday).

m-Xylylenebis(Cusalprn) (**7**). A methanolic solution of **3** (1.25 g, 5 mm) (20 ml) is added to a refluxing solution of bis(salicylaldehyde)copper(II) dihydrate (3.06 g, 10 mm) in methanol (100 ml). The solution is refluxed twenty hours, cooled and filtered yielding **7** as a green solid, (2.0 g, 50%). Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{CuO}_4$ : C, 62.43; H, 5.00; Cu, 6.94; Cu, 15.73. Found: C, 62.68; H, 5.00; Cu, 6.90; Cu, 15.42. IR:  $\nu_{\text{C-N}}$  1605;  $\nu_{\text{aromatic}}$  1533  $\text{cm}^{-1}$ .

VIS ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  600 nm ( $\epsilon$  495).  $\mu_{\text{eff}}$  1.92 B.M./metal center (Faraday). 1.49 B.M./metal center (Evans).

[2,2'-(2-Benzyl-1,3-propanediyl)bis(nitrimethylidene)-bis(phenolato)nickel] (**Nisal-3z-prn**) (**8b**). Salicylaldehyde (0.3 g, 2.4 mm) and **3** (0.2 g, 1.2 mm) are refluxed in ethanol (10 ml) for fifteen minutes.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.20g, 1.2 mm) is then added and the solution refluxed 15 hours. The solution is cooled and filtered yielding **8b** as brown crystals (0.20 g, 39%). Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{NiO}_4$ : C, 67.17; H, 5.17; Ni, 6.53. Found: C, 67.26; H, 5.41; Ni, 6.60. IR (KBr):  $\nu_{\text{C-N}}$  1610;  $\nu_{\text{aromatic}}$  1535  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 6.3-7.3 (m, 15H, aromatic, imine CH), 3.1-3.7 (m, 4H,  $\text{CH}_2\text{-N}$ ) ( $J_{\text{geminal}}$  = 13 Hz,  $J_{\text{H-CH}_2\text{-C}}$  = 6 Hz), 2.5-2.6 (d, 2H, benzylic) ( $J_{\text{benzylic-methine}}$  = 7 Hz), 2.1-2.4 (m, 1H, methine).

#### Formation and observation of nickel(II) complexes.

[m-Xylylenebis(Nisalprn)] $^{2-}$ . A suspension of m-xylylenebis(Nisalprn), **5**, (0.25 g, 0.32 mm) in dry, deoxygenated THF (50 ml) is placed over sodium amalgam under a nitrogen atmosphere. The yellow suspension gradually becomes deep blue and is transferred using cannulae to a second flask under nitrogen. This blue THF solution is then used in subsequent experiments. UV/VIS(THF):  $\lambda_{\text{max}}$  675 nm ( $\epsilon$  2000), 470 nm ( $\epsilon$  1700), 360 nm ( $\epsilon$  12,000).

CO adduct. Carbon monoxide is bubbled through the blue nickel(II) solution for two minutes causing the solution to turn green. IR(THF):  $\nu_{\text{CO}}$  2045  $\text{cm}^{-1}$ .

$\text{CH}_3\text{NC}$  adduct Addition of excess methyl isocyanide to the blue nickel(II) solution results in the formation of yellow solution. IR(THF):  $\nu_{\text{CN}}$  2165, 2070  $\text{cm}^{-1}$ .

## Results and Discussion

**Ligand Synthesis.** The ligand used to prepare the binuclear complexes studied in this paper is made by the Schiff base condensation of four equivalents of salicylaldehyde with *m*-xylylenedibis(2-(1,3-propanediamine), **3**). The synthesis of this new tetra-amine (**3**) is accomplished by the following route. The condensation of isophthalaldehyde with two equivalents of malononitrile produces *m*-xylylenedibisammonitrile (**1**). The reduction of **1** by TEAF, followed by Hg<sub>2</sub>-TfH reduction produces the desired compound,

*m*-xylylenedibis(2-(1,3-propanediamine)). Infrared analysis of the product shows the presence of a primary amine ( $\nu_{NH_2}$ , 3350  $cm^{-1}$ , 3280  $cm^{-1}$ ). The amine is soluble in water and alcohol but relatively insoluble in other organic solvents. Distillation at reduced pressure (0.001 mm Hg, 150°C) yields **3** as a colorless oil. Although not analytically pure, the formation of **3** is confirmed by its proton NMR in either D<sub>2</sub>O or *d*<sup>6</sup>-methanol along with the isolation of binuclear complexes prepared from this tetra-amine compound. The binuclear complexes **5-7** are prepared by minor modifications to the reported synthetic procedures for their mononuclear analogues, **9a-10**, respectively.

**Nickel complexes.** The reaction of nickel(II)bis(salicylaldehyde) with **3** in refluxing methanol produces the binuclear nickel complex (**5**) in 83% yield. Complex **5**, isolated as a brown solid, analyzes correctly for the dihydrate, and is soluble in tetrahydrofuran, dichloromethane, chloroform and dimethylsulfoxide, giving yellow-to-light brown solutions. The mononuclear analogue, **9a**, which is also a brown solid, gives similarly colored solutions.

A second mononuclear analogue, complex **9b** (Nisal-bz-prn), is prepared by the addition of nickel(II)chloride to an ethanolic solution of salicylaldehyde and 2-benzyl-1,3-diaminopropane, and is isolated as a brown crystalline solid in 39% yield.

All these nickel complexes, **5**, **9a** and **9b**, have similar spectral properties. The infrared spectra of Nisal-bz-prn (**9a**) and *m*-xylylenedibis(Nisalprn) (**5**) both show strong absorption bands at 1610 and 1535  $cm^{-1}$  (C=O) while Nisalprn (**9a**) exhibits IR bands at 1616 and 1543  $cm^{-1}$  (nu11).<sup>14</sup> The visible absorption spectrum of *m*-xylylenedibis(Nisalprn) has an absorption maximum at 600 nm (shoulder) while Nisalprn has a similar maximum of 595 nm.<sup>18</sup> The extinction coefficients of the two complexes are both small ( $\epsilon$  = 136 for **5** and  $\epsilon$  = 80 for **9a**) typical of d-d transitions. Solid state susceptibility measurements show that **5** is diamagnetic.

The 400 MHz proton NMR spectrum of *m*-xylylenedibis(Nisalprn), **5**, is shown in Figure 2. The aromatic protons appear as a series of multiplets in the 6.5 to 7.3 ppm region along with a 7.18 ppm singlet due to the imine CH. Decoupling experiments allow the unambiguous assignment of each of the arene resonances. In addition, the benzylic hydrogens appear as a doublet ( $J$  = 7.6 Hz) at 2.65 ppm, split by the methine hydrogen, H<sub>K</sub>. The inequivalent methylene hydrogens, H<sub>I</sub> and H<sub>J</sub>, of the propanediamine chelate ring appear at 3.57 and 3.28 ppm as doublets of doublets, split by each other ( $J_{geminal}$  = 13.1 Hz) and by H<sub>K</sub> ( $J_{vicinal}$  = 6.2, 6.4 Hz). The methine hydrogen, H<sub>K</sub>, appears as a multiplet at 2.32 ppm. The proton NMR spectrum and the detailed spectral assignments thus provide conclusive evidence for the binuclear structure of complex **5**, *m*-xylylenedibis(Nisalprn). Additional support is also found in the proton NMR spectrum of Nisal-bz-prn, **9a**, which closely resembles that of the binuclear nickel complex **5**. The aromatic and imine CH resonances appear in the 6.3 to 7.4 ppm region. The benzylic hydrogens appear at 2.55 ppm split into a doublet by the methine hydrogen ( $J$  = 7 Hz). The methylene hydrogens of the propanediamine ring are once again inequivalent and appear as two doublets



of doublets at 3.2 and 3.9 ppm ( $J_{\text{H-H}} = 13 \text{ Hz}$ ,  $J_{\text{H-C}} = 6 \text{ Hz}$ ), while the acetone hydrate appears as a multiplet at 2.26 ppm.

Both  $\text{Mn}(\text{salprn})$  (**4a**) and  $m\text{-xylonebis}(\text{Mn}(\text{salprn}))$  (**5**) exhibit quasireversible reductions in DMF as demonstrated by cyclic voltammetry. (See Table I.) Complex **4a** shows a reduction wave at  $-1.47 \text{ V}$  while the binuclear nickel complex exhibits a reduction wave at  $-1.47 \text{ V}$ . Each wave is due to the  $\text{nickel(II)-nickel(II)}$  couple. Controlled potential coulometry of **4** in DMF at  $-1.05 \text{ V}$  shows that one electron per metal center is passed. It has been reported that reduced macrocyclic nickel complexes react with CO to give  $\text{Ni(I)-CO}$  adducts.<sup>19</sup> Reduction of **4** in THF using 25 sodium amalgam produces a deep blue solution. The visible spectrum of this  $\text{nickel(II)}$  solution shows a strong absorption and 675 m ( $\epsilon 2000$ ) compared to the weak absorption at 600 m ( $\epsilon 130$ ) for the  $\text{nickel(II)}$  complex (**5**). When the blue  $\text{nickel(II)}$  solution is placed under an atmosphere of carbon monoxide, the solution becomes green and its IR spectrum shows a stretch at  $2045 \text{ cm}^{-1}$  indicating the formation of a  $\text{nickel(I) carbonyl}$  adduct. In a separate experiment, the introduction of excess methyl isocyanide to the blue  $\text{nickel(II)}$  solution causes the color to change to yellow, and the infrared spectrum exhibits stretches at 2165 and  $2070 \text{ cm}^{-1}$  corresponding to free and coordinated methyl isocyanide, respectively.

**Manganese Complexes.**  $m\text{-Xylonebis}(\text{Mn}(\text{salprn}))$ , **5a**, is prepared by the reaction of manganese acetate and salicylaldehyde with **2** under a nitrogen atmosphere, and is isolated as a yellow solid in 60% yield. The reaction must be carried out under an inert atmosphere since the resulting manganese Schiff base complex is easily oxidized in solution. Once the complex is filtered and dried, it is moderately stable towards air oxidation, but does gradually darken over a period of several weeks. The binuclear manganese complex

analyses correctly for the trihydrate, and is paramagnetic both in solution and in the solid state. Measurement of the magnetic moment of **5a** in DMF solution using the Evans NMR method gives a value of  $\mu_{\text{eff}} = 4.95 \text{ B.M.}$  per metal center, consistent with a high spin  $\text{manganese(III)}$  complex, thus providing evidence for the ease of air oxidation of the manganese center in solution. Using the same method, a magnetic moment of  $5.01 \text{ B.M.}$  is obtained for  $\text{Mn}(\text{salprn})$ , **2a**. Determination of the solid state magnetic moment by the Faraday method gives  $\mu_{\text{eff}} = 5.47 \text{ B.M.}$  per metal center for **5a** and  $\mu_{\text{eff}} = 6.01 \text{ B.M.}$  for **2a** (lit  $\mu_{\text{eff}} = 5.93 \text{ B.M.}$ ).<sup>20</sup> The lower magnetic moment of **5a** as determined by this method may be due to increased interactions between the  $\text{Mn(II)}$  centers in **5a** resulting from its binuclear structure. However, other factors such as partial oxidation of **5a** in the solid state relative to **2a** cannot be ruled out at this time.

The manganese complexes **5a** and **2a** have similar infrared spectra typical of transition metal Schiff base complexes. Quasireversible oxidations in DMF are observed for **5a** and **2a** when examined by cyclic voltammetry.  $\text{Mn}(\text{salprn})$  exhibits a quasireversible wave at  $-0.24 \text{ V}$  ( $E_{1/2}$ ) while  $m\text{-xylonebis}(\text{Mn}(\text{salprn}))$ , **5a**, has a wave at  $-0.25 \text{ V}$ . These waves are due to the  $\text{manganese(III)-manganese(II)}$  couple.

Two other binuclear manganese complexes have been synthesized<sup>21</sup> and examined electrochemically. Electrochemical properties of these manganese complexes are shown in Table I. The reduction potentials for complexes **6a** and **6c** are similar while **6b** is shifted significantly more positive. This observation is readily explained by the electron withdrawing properties of the nitro-substituent of **6b**, which causes a decrease in electron density at the metal centers thereby stabilizing the  $\text{manganese(II)}$  oxidation state relative to that of  $\text{manganese(III)}$ .

**Copper Complexes.**  $m$ -Toluenedithiocarbamate ( $\text{Cu}(\text{mtc})_2$ ),  $\text{Z}$ , is prepared by the reaction of copper(II)acetate dihydrate with  $\text{Z}$  and is obtained as a green solid in 80% yield. No yield was reported for  $\text{Cu}(\text{salpn})_2$  (10). The binuclear complex analyses correctly for the mononuclear and is paramagnetic both in the solid state and in DMSO solution. Measurement of the magnetic moment of  $\text{Z}$  in the solid state gives a value of  $\mu_{\text{eff}} = 1.92$  B.M. per metal center consistent with copper(II). The solid state moment,  $\mu_{\text{eff}}$ , determined for  $\text{Cu}(\text{salpn})_2$  is 1.85 B.M. The solution magnetic moments were determined in DMSO by the Evans method yielding values of  $\mu_{\text{eff}} = 1.49$  B.M. and 1.79 B.M. for  $\text{Z}$  and  $\text{10}$  respectively. The reduced moment for the binuclear system  $\text{Z}$  relative to the mononuclear complex  $\text{10}$  again suggests the possibility of increased magnetic interactions for the former, presumably due to the closer average proximity of two metal centers in a binuclear complex relative to the separation of two mononuclear complexes in solution. The copper complexes  $\text{Z}$  and  $\text{10}$  exhibit similar infrared spectra which are consistent with copper Schiff base complexes. The visible spectra show similar absorption maxima. For the binuclear complex,  $\lambda_{\text{max}} = 605$  nm ( $\epsilon$  495) while for  $\text{Cu}(\text{salpn})_2$ ,  $\lambda_{\text{max}} = 603$  nm ( $\epsilon$  240). Cyclic voltammetry of  $\text{Z}$  in DMSO shows the presence of a poorly defined irreversible reduction wave at -1.4 V. Similar behavior is exhibited by its mononuclear analogue  $\text{Cu}(\text{salpn})_2$ ,  $\text{10}$  ( $E_{\text{red}}^{\text{irrev}} = -1.3$  V).

#### SUMMARY

From the preceding discussion it is seen that the spectral and physical properties of the binuclear complexes are very similar to those of their mononuclear analogues. The visible spectra of the nickel and copper binuclear complexes are nearly identical to the corresponding mononuclear nickel and copper complexes. Electrochemical studies show that the redox

properties of the binuclear nickel and manganese complexes ( $\text{Ni}(\text{dgt})_2$ ) are very similar to the mononuclear complexes of nickel and manganese ( $\text{Ni}(\text{dgt})_2$ ). The presence of two metal centers in the binuclear complexes does not appear to affect the reduction potentials of the nickel or manganese complexes, but the peak separations do appear to be slightly larger for the binuclear complexes compared to their mononuclear analogues (see Table I). However, no splitting of the waves into two components is observed for the binuclear complexes. This observation leads us to two possible conclusions. (1) The metal centers are sufficiently insulated from one another to prevent significant electronic interactions between them. (2) While weak electrostatic interactions between the metal centers may exist in the binuclear complex, their effects are not observable by cyclic voltammetry. Theory predicts that even in the case of molecules containing multiple, noninteracting redox centers, the successive electron transfers should follow a statistical separation of formal potentials.<sup>22</sup> For a two center system this separation should be 36 mV. We might therefore expect a slight broadening of the cv waves of the binuclear complexes compared to their mononuclear analogues which is in fact the case. These observations suggest that for the binuclear complexes reported here, the two metal centers are for the most part electronically insulated. There does, however, seem to be enough conformational flexibility in the ligand framework to allow a "face-to-face" approach of the two metal centers. This may be evidenced by the reduced magnetic moments in solution of the binuclear complex  $\text{Z}$  relative to its mononuclear analogue  $\text{10}$ . Attempts to obtain more direct evidence of the conformational flexibility of these binuclear systems, such as through the formation of adducts in which a common substrate is coordinated to both metal centers, are in progress. We expect

that binuclear complexes of the type reported here will be capable of storing  
storing two units of charge (electrons or holes) via one electron redox  
processes for each metal center, and then transferring these units of charge  
to a commonly bound substrate as redox activated catalysts.

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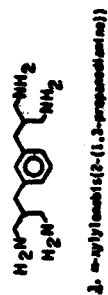
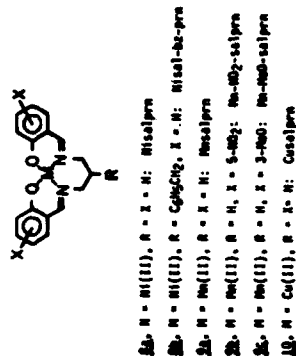
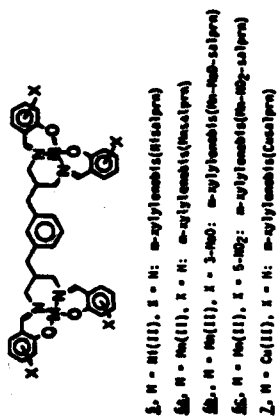
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21. Compounds **2b** and **2c** are prepared by atom modification of the procedure for the synthesis of **2a**, substituting 3-methoxy- or 5-methoxy-salicylaldehyde. Similarly, compounds **2d** and **2e** are prepared by the same method as **2a** using the substituted salicylaldehydes in place of salicylaldehyde. These complexes have been synthesized but not obtained analytically pure.
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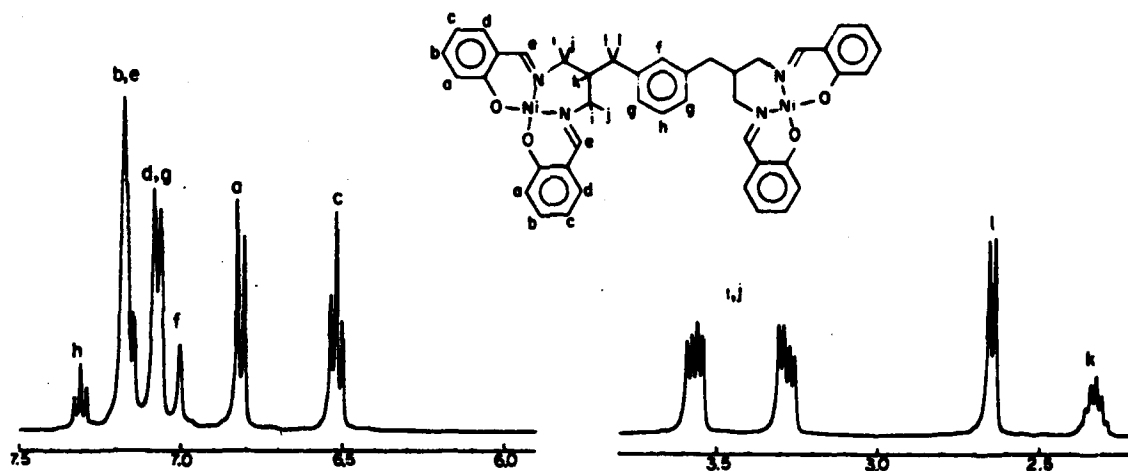
Table 1. Electrochemical Data for the Dinuclear and Mononuclear Complexes<sup>a</sup>

Complex	E <sub>1/2</sub> , V	ΔE <sub>p</sub> , mV	i <sub>p</sub> <sup>2</sup> /i <sub>p</sub> <sup>0</sup> , a	scan rate, mV/s
m-xylylenediis(Nisalprn) <b>2</b>	-1.47	160	1.04	200
Nisalprn <b>2a</b>	-1.46	130	.97	200
m-xylylenediis(Musalprn) <b>2a</b>	-0.25	130	1.07	200
Musalprn <b>2a</b>	-0.24	90	1.03	200
m-xylylenediis(Mn-MO <sub>2</sub> -salprn) <sup>b</sup> <b>2b</b>	-0.11	100	.95	50
Mn-MO <sub>2</sub> -salprn <sup>b</sup> <b>2b</b>	-0.12	105	1.00	50
m-xylylenediis(Mn MeO-salprn) <sup>b</sup> <b>2c</b>	-0.20	110	1.13	50
Mn MeO salprn <sup>b</sup> <b>2c</b>	-0.23	91	1.08	100
m-xylylenediis(Cusalprn) <b>2</b>	-1.4 <sup>c</sup>	--	--	500
Cusalprn <b>2d</b>	-1.3 <sup>c</sup>	--	--	500

<sup>a</sup> DMSO solution, complex concentration 10<sup>-3</sup> M, supporting electrolyte TBAP (0.1 M), platinum electrode (296 K). <sup>b</sup> Reference 21. <sup>c</sup> Irreversible wave, glassy carbon electrode, supporting electrolyte TEAP (0.1 M). <sup>d</sup> The cyclic voltammetric peak-to-peak separation.

Figure 1: Labeling scheme and nomenclature.

Figure 2: 400-MHz <sup>1</sup>H NMR spectrum of m-xylylenediamine (Nisalpm). 5.



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